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Structure Development During Converging Flow of
a Liquid Crystal Dispersed Two-Phase Fluid

by

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The flow dynamics of liquid crystal (LC)-dispersed two phase fluids were studied in order to determine the relationships between the deformation of the dispersed phase (D), the weber number (We) and the viscosity ratio of the two phases (k). A flow visualization apparatus consisting of a glass capillary with aconical converging entrance and a video system was constructed and used to measure droplet deformation in the entrance region (extensional flow) and in the capillary (shear flow).

The systems studied included p-ethoxybenzyline-p-butylanine (EBBA) dispersd in three Newtonian fluids [50, 80, and 100% glycerin (aq)] and three viscoelastic, non-Newtonian fluids [0.35. 1.0, and 1.5% polyacrylamide (aq)]. The data were compared with the theoretical predictions for non-LC containing two phase fluids by Reijden-Stolk and Sara. D increased with increasing We and it appeared that LC droplets may experience more deformation than isotropic fluid dispersions for comparable values of We and k.

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The relaxation of the extended droplets was studied in the capillary region, and the effectof the extension in the entrance persisted to relatively long axial distances. These results have potential utility in the design of processes for optimizing the deformation of the LC or liquid crystalline polymer phase in a polymer blend. Such compositions are being examined as self-reinforcing materials.

STRUCTURE DEVELOPMENT DURING CONVERGING FLOW OF
A LIQUID CRYSTAL DISPERSED TWO-PHASE FLUID

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INTRODUCTION.

Recently, the use of liquid crystals (lc's) and liquid crystal polymers (lcp's) as reinforcements for thermoplastics has increased due, primarily, to the ability to impart a high degree of molecular order to these materials during processing. Huh (1) and Weiss et. al. (2) have shown that it is possible to obtain improved mechanical properties by adding an lcp to polystyrene. This improvement was the result of obtaining highly elongated lcp fibers throughout the polystyrene matrix by drawing the blend extrudate which reinforced the ps in a fashion analogous to that of rigid glass or carbon fibers. Han (3) and Reijden-Stolk and Sara (4) have shown that dispersed phase deformation, D, is dependent on the Weber number, $We_{\dot{\epsilon}}$, and inversely dependent on viscosity ratio, k, for two phase blends of isotropic fluids in converging flow. These variables are dimensionless and are defined as:

$$D = \frac{L-B}{L+B},$$

$$We_{\dot{\epsilon}} = \frac{\dot{\epsilon}\,\eta_c\, r_d}{\sigma},$$

$$k = \frac{\eta_d}{\eta_c},$$

where L and B are, respectively, the length and width of the deformed droplet phase, $\dot{\epsilon}$ is the rate of elongation, r_d is the radius of the initially undeformed droplet, σ is the interfacial tension of the two phase system, and η_d and η_c are, respectively, the dispersed phase and continuous phase viscosity.

Due to the ability to use lc's and lcp's as reinforcements and to the lack of fundamental data on flow dynamics of lc dispersed two phase fluids the present study was undertaken. Specifically, our objectives were, for single lc droplets bounded by an immiscible fluid, to establish a relationship between D, $We_{\dot{\epsilon}}$, and k in a converging flow field, establish conditions for droplet breakup, and determine a characteristic relaxation time of the lc droplets in pre-extensional shear flow. A flow apparatus was designed and constructed to accomplish these objectives.

EXPERIMENTAL

The lc droplet phase used in the study was p-Ethoxybenzylidene p-Butylaniline (EBBA). It was purchased from the Chemical Dynamics Corporation, and had the following structure:

CH3-CH2-O-⬡-CH=N-⬡-(CH2)3-CH3
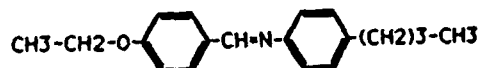
Six different matrix phases were used to generate different material parameters. They were 50, 80, and 100 wt. % glycerin (aq.), and 0.35, 1.0, and 1.5 wt. % polyacrylamide (aq.). Glycerin was purchased from Fisher Scientific and polyacrylamide was supplied by American Cyanamid.

Transition temperatures of the EBBA were determined with a Perkin Elmer Differential Scanning Calorimeter (DSC) Model 2, and the mesophase texture was established with a hot stage microscopy system with cross polars comprised of a Nikon Labophot-Pol microscope, a Nikon AFX camera system, and a Linkham TH 600 hot stagecontrolled by a Linkham TMS 90 heat controller.

Rheological measurements were made with a Rheometrics System IV Mechanical Spectrometer using the 50 mm cone and plate attachment, and with a Brookfield LVTDV-II Viscometer using the small sample adapter.

Interfacial tension measurements were made with a pendant drop apparatus developed in the lab of Dr. Jeff T. Koberstein. This apparatus consisted of a metal chamber the temperature of which was controlled by an Omega CN-2012 programmable temperature controller, a NEC TI-22A video camera with a Cannon FD 50-300 mm zoom lens, an IBM PC with a Tecmar Video Van Gogh board for data acquisition, frame grabbing, and image digitization, and a Panasonic WV-5410 video monitor. More information about this system is available in Anastasiadis et. al. (5).

Droplet deformation studies were made with a flow apparatus developed by the authors. It was comprised of two major sections: a flow system and a video system. The primary feature of the flow system was a glass capillary tube which was fastened into a plexiglass cell by O-ring fittings at either end of the tube. The capillary tube was comprised of three sections: an entrance region, a conical converging region, and a capillary tube. The entrance region had an inside diameter of 2.5 cm. and a length of 30 cm. The length of the conical section was 12 cm. and had a total angle of 20 degrees. The capillary region had an inside diameter of 2 mm and a length of 60 cm. The matrix fluid was pumped with a Cole-Parmer 7617-60 Magnetic Drive Pump through the capillary from a reservoir heated by a Braun Termomix 1420 Bath, and the flow rate was monitored by a Manostat 36-541-125 flowmeter. Water was heated and circulated through the plexiglass jacket by a Lauda CS-20 Bath to maintain a constant temperature of 45° C. After steady state conditions were established droplets of EBBA of known volume were injected into the flowing matrix at the tube centerline by using a Hamilton series 700 syringe fitted with a Hamilton PB-600 repeating dispenser which was enclosed in a chamber the temperature of which was maintained at 45° C by an air blower. The temperature of the matrix fluid entering the glass tube was monitored by an Omega Engineering Model 199 digital thermometer. The temperature of the circulating water was monitored at the inlet and outlet of the plexiglass cell by an Omega 199 RTD, and an Omega 660 digital thermometer, respectively. Droplets could then be recorded by the Panasonic AG-1950 video tape recorder (vtr) and monitored by the Panasonic WV-5410 video monitor at any vertical position in the capillary by adjusting the vertical position of the NEC TI-23A video camera. More information about this system is available in Yanisko (6).

RESULTS

Prior to performing the deformation studies thermal, rheological, and interfacial characterization was necessary. The crystal to nematic

(K-N) and nematic to isotropic (N-I) transitions of EBBA were 37 and 78° C, respectively. A threaded schleiren structure, typical of nematic lc's, was evident in microphotographs of EBBA taken between crossed polars at 45° C. the shear rate dependent viscosity of EBBA is illustrated in Figure 1, and may be divided into two regimes: a shear thinning region at lower shear rate, and a Newtonian region at high shear rate. This behavior is typical of liquid crystals. The shear thinning, as explained by Onogi and Asada (7), is due to destruction of a polydomain structure rather than chain uncoiling as is the case in polymer melts or solutions. The destruction of the polydomain structure proceeds as shear rate is increased until a monodomain forms in which wide scale molecular orientation exists. Each glycerin solution, and each polyacrylamide solution exhibited Newtonian and pseudoplastic behavior, respectively, over the range of shear rates studied. Elastic behavior was observed for the polyacrylamide fluids only and increased with concentration and shear rate. The interfacial tension of each two phase system studied is listed in Table 1. Relative to other two phase liquid systems these values are high.

The dependence of D on We_ε is illustrated in Figure 2 for constant k. On this graph predicted and measured values of D are plotted for EBBA drops in a glycerin matrix phase filmed at the cone exit - the location at which the extensional rate is greatest. The predictions were made from the method of Reijden-Stolk and Sara (4) in which D is given by:

$$D = 3 \frac{F(k)}{k} \exp^Q E_1(Q).$$

where

$$F(k) = \frac{5(19k + 16)}{171(k + 1)},$$

$$Q = \frac{40}{57 k We_\varepsilon},$$

$$E_1(Q) = \int_Q^\infty (\frac{\exp^{-y}}{y}) dy.$$

For both the measured and predicted values D increases as We_ε increases. Agreement between measured and predicted values of D is fair with the predictions of D being less than the measured values for $We_\varepsilon > 0.1$. This suggests that lc drops may experience more deformation than isotropic drops bounded by a Newtonian fluid in extensional flow for these conditions.

Upon exiting the conical region of the flow tube the droplets relaxed as they proceeded through the capillary tube due, primarily, to the absence of an extensional flow component. This effect is illustrated in Figure 3 in which D vs. position in the capillary is plotted for droplets of EBBA in a glycerin matrix phase for $We_\varepsilon = 0.068$. Note that complete relaxation of the lc drop did not occur even after travelling 30 cm. into the capillary. This is promising because in order to maximize the strength properties of an lc or lcp reinforced composite, large aspect ratios of the dispersed phase are needed. An attempt was made to

determine a characteristic relaxation time of the EBBA by fitting the data to an equation of the form:

$$D = D_{c} e^{-t/\tau}.$$

where D is the deformation parameter, D_0 is the deformation paramter at the cone exit, t is time, and τ is a relaxation time. A linear plot of ln D vs. t should yield a vertical intercept of ln D_0, and a slope of $- 1/\tau$. Very poor agreement was obtained between the curve of the equation and the data. A possible explanation is that relaxation was inhibited by a wall effect due to the large size of the droplets relative to the capillary diameter. Regardless, it is evident that the data cannot be modelled by a single relaxation time.

For certain conditions droplet deformation was followed by droplet breakup as the droplet exited the cone. This is illustrated in Figure 4. These conditions are in very good agreement with Han's (3) observations of droplet breakup in two phase blends of isotropic fluids during conical converging flow.

For k= 0.11 and We_{ϵ} = 0.242 the extension of the droplet at the cone exit, breakup as it exits the cone and subsequent relaxation into a bullet shape in the capillary downstream of the cone exit are illustrated in Figure 5 for droplets of EBBA.

ACKNOWLEDGEMENTS

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3. C.D. Han and H.B. Chin, J. Rheol., 23, 557, 1979.
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7. S. Onogi and T. Asada, RHEOLOGY, VOL. 1, 127, Plenum Press, NY, 1980.

Table 1: Interfacial tension data.

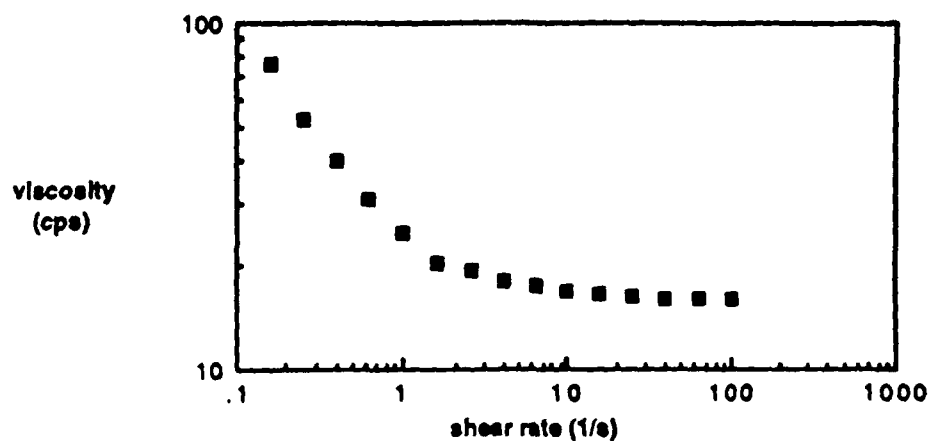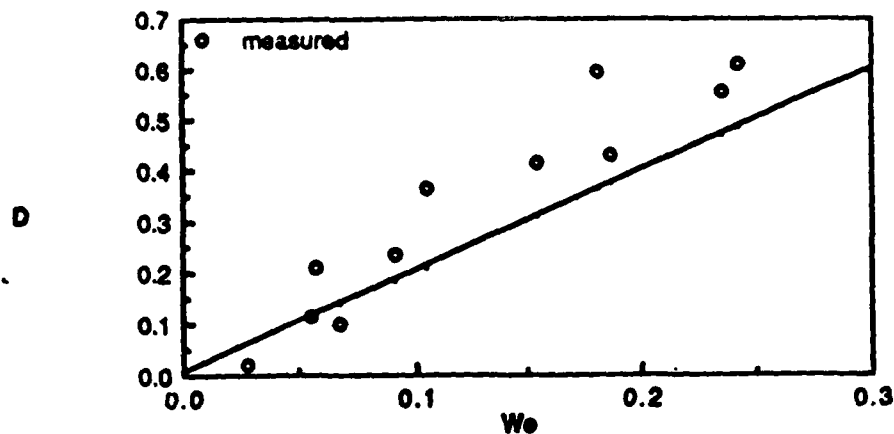| Two phase system	Interfacial tension (dyne/cm)
EBBA / glycerin	13.6
EBBA / 80 wt. % glycerin	15.3
EBBA / 50 wt. % glycerin	15.7
EBBA / 1.5 wt. % pam	19.3
EBBA / 1.0 wt. % pam	18.7
EBBA / 0.35 wt. % pam	18.4

Figure 1: Viscosity behavior of EBBA.
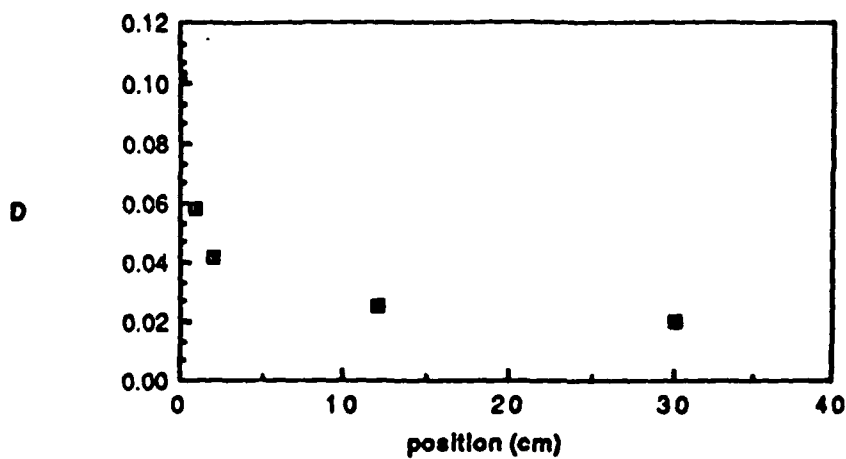

Figure 2: D vs. We for EBBA droplets, k = 0.11.

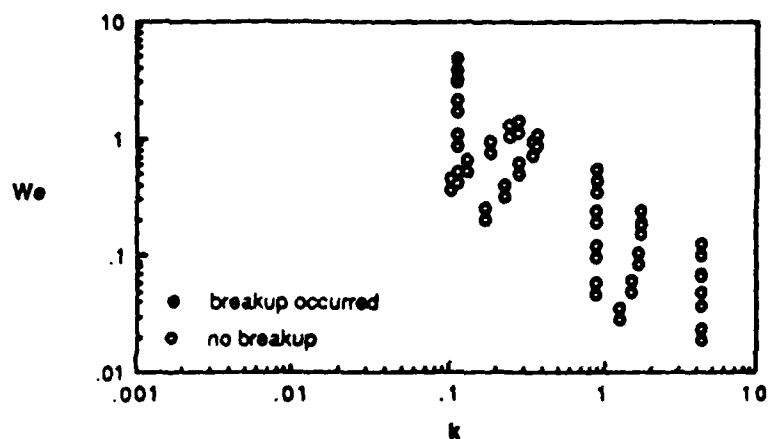Figure 3: D vs. capillary position, k = 0.11, We = 0.068.
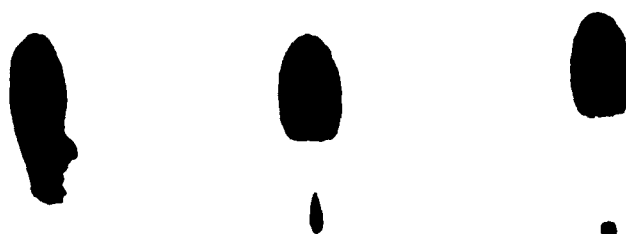

Figure 4: Droplet breakup criteria.

Figure 5: Deformed EBBA droplet (k = 0.11, We = 0.242);
a. at cone exit, b. 1 cm. into capillary, c. 2 cm. into capillary.